Graphene: High Thermal Conductivity at the Nanoscale?

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Abstract: Over the last decade, the high thermal conductivity of graphene flakes and carbon nanotube (CNTs) at the nanoscale has received much attention in the heat dissipation of microelectronic devices. But Molecular Dynamics (MD) and Finite Element Models (FEM) analysis in support of high thermal conductivity based on classical physics are no longer valid at the nanoscale because the atoms in nanostructures are assumed to have temperature, when in fact the Planck law denies atoms at the nanoscale the heat capacity to conserve heat by an increase in temperature. Indeed, phonons dependent on temperature implicit in MD and FEM do not even exist at the nanoscale. In this regard, the simple QED method of nanoscale heat transfer based on the Planck law conserves heat by the emission of EM radiation instead of increases in temperature. Under steady laser heating at the center of a graphene flake, the in-plane thermal conductivity assumed proportional to the laser heat is highly overstated as soft X-ray emission normal to flake is not included as a significant heat loss. Similarly, most heat in CNTs is dissipated across the diameter making thermal conductivity based on heat transfer along the length also highly overstated. In contrast, the thermal conductivity of silicon nanowires (NWs) is not measured by assuming heat only flows along the NW length, but rather simply measures the temperature difference across the wire length, the consequence of which is the thermal conductivity of silicon at the nanoscale is not higher than bulk, but rather at least 100X lower than bulk consistent with simple QED.

Keywords: Graphene flakes, carbon nanotubes, nanowires, thermal conductivity, Planck law, simple QED

I. INTRODUCTION

Over the past decade, the discovery of graphene comprising a 2D layer of single atoms arranged in a honeycomb lattice has received considerable attention [1] as a promising material for future electronic circuits. Shortly thereafter, the promise of graphene attracted research [2] on the related thermal conductivity of 1D carbon nanotubes (CNTs) as interconnects in integrated circuits, both finding commonality in the nanoscale.

Later, the thermal conductivity of single atom 2D layers of graphene flakes [3] gained much interest as a non-contact method used was based on confocal micro-Raman spectroscopy as illustrated in Fig. 1.
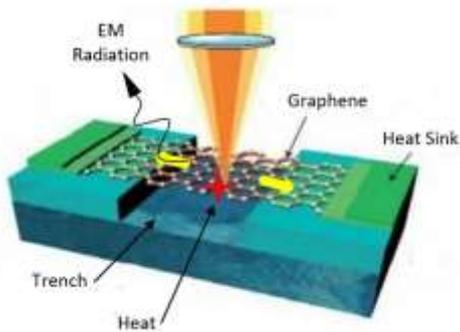

Figure 1. Thermal Conductivity Test

The Raman G peak temperature was used to monitor the temperature change produced by the variation of the laser excitation power focused on a graphene layer in Fig. 1. The graphene is suspended over a trench. Heat (red star) in the middle flows outward in-plane (yellow arrows) to heat sinks. The heat Q transferred to the heat sinks excludes the heat loss by EM emission (black arrows) from the graphene to the surroundings.

Since heat loss to contact with the trench edges is negligible, the graphene in-plane thermal conductivity K assumes all laser heat Q is transferred to the heat sinks giving,

$$K = (L/2S) \cdot (\Delta Q/\Delta T)$$

where L and S are the length and area of the suspended graphene, and $\Delta Q/\Delta T$ is the change in Q for a change in temperature. Here, S = wd with w and d the layer width and thickness. At room temperature, the single layer graphene was found to have K = 4800 to 5800 W/mK. Compared to bulk carbon having 2000 W/mK the nanoscale showed a significant increase.

The literature at that time generally showed carbon at the nanoscale had higher thermal conductivity than bulk carbon. Indeed, bulk crystalline diamond [4] gives K ~ 1000–2200 W/mK, multiwall CNTs [5] give 3000 W/mK, and K ~ 3500 W/mK for single-wall CNTs [2].

Theoretical estimates of CNT thermal conductivity mostly support [3] the experimental results, although some discrepancy exists. Molecular dynamics (MD) simulations [6] of diamond CNT give very high K ~ 6,600 W/mK by assuming the Tersoff potential for temperature dependence for a crystal at 300 K. The MD assumed cells across the diameter, but periodic boundary conditions along the length consistent with classical physics allow finite heat

capacity which is justified as the length L > a few microns, but is invalid through the thickness. Regardless, the MD results are consistent with reports that at 104 K, the thermal conductivity of diamond 410 W/cm K, or 41,000 W/mK which is the highest measured thermal conductivity [7] for a solid above liquid nitrogen temperature.

Experimental and theoretical estimates of thermal conductivity of graphene and carbon at the nanoscale were generally considered controlled by phonons. Today, the state of graphene [8] as of 2019 suggests the high thermal conductivity of graphene first reported [2,3] is still based on phonons guiding heat transfer at the nanoscale.

Indeed, the MD simulation and Abaqus finite element analysis [9] reported in [8] assume classical physics in the heat transfer of nano-thickness graphene flakes which also give far higher thermal conductivity than bulk consistent with work [2-7] a decade ago.

But there is a problem.

Well before the seminal findings [2,3] of high thermal conductivity of graphene and carbon at the nanoscale, silicon NWs were not found [10] to have enhanced thermal conductivity over bulk, but rather 100X less than bulk. Even today, the thermal conductivity of silicon NWs [11,12] is at least 2 orders of magnitude lower than bulk values. Theoretically, silicon should be no different than carbon materials at the nanoscale as both transfer heat by a ballistic process driven by infrequent phonon collisions compared to classical diffusive processes driven by frequent phonon collisions. Yet, nanoscale silicon is characterized by size dependence of the effective thermal conductivity (ETC) while carbon-based materials are not.

II. PURPOSE

The purpose of this paper is to propose simple QED heat transfer [13] explains the stark differences between silicon and carbon-based materials at the nanoscale. Comparisons are made to experimental data and analytical predictions in the literature.

II. THEORY

Simple QED is a nanoscale heat transfer process based on the Planck law [14] of quantum mechanics (QM) differing significantly from that of classical physics. Research in nanoscale heat transfer [15-17] has been reported. But despite advances, there are still challenges in understanding the mechanism of nanoscale thermal transport. Perhaps, researchers have not appreciated the significant difference between classical physics and the Planck law with regard to the heat capacity of the atom illustrated in Fig. 1.
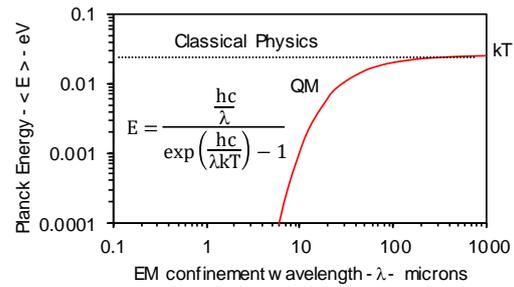

Figure. 1: Planck law of QM at 300 K
In the inset, E is Planck energy, h Planck's constant, c light speed, k Boltzmann's constant, T temperature, and λ the EM wavelength.

The Planck law at 300 K shows classical physics allows the atom to have constant kT heat capacity over all EM confinement wavelengths λ. QM differs as the heat capacity of the atom decreases for λ < 200 microns, and vanishes at the nanoscale for λ < 100 nm.

Indeed, simple QED by the Planck law denies atoms in nanostructures the heat capacity to increase in temperature upon the absorption of heat. QED stands for quantum electrodynamics, a complex theory based on *virtual* photons advanced by Feynman [18] and others. Simple QED is a far simpler theory that only requires the heat capacity of the atoms in nanostructures to vanish allowing conservation to proceed by the creation of *real* photons comprising EM waves that stand across the nanostructure.

Similar to atom quantum states of electrons in discrete orbitals, simple QED quantum states are dependent on the dimension of the nanostructure over which the EM waves stand. The Planck energy E of a photon standing across a distance d is given by the time τ for light to travel across and back, $\tau = 2d/(c/n)$, where n is the index of refraction of the nanostructure Hence, the Planck energy E of the simple QED photons is, $E \sim h/\tau$ and wavelength $\lambda = 2nd$,

$$E = \frac{hc}{2nd}$$

The laser heating Q of a nanoparticle (NP) of diameter d by a laser having wavelength $\lambda_o \gg d$ immerses the NP in Q radiation to emit UV is illustrated in Fig. 2.
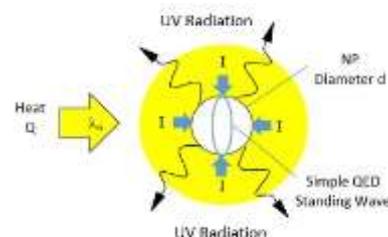

Figure 2. Laser Heating of a NP

The simple QED standing wave in the NP is shown under EM confinement by a Poynting vector of thermal momentum I (blue arrows) from the difference in temperature between the thermal surroundings at 300 K and the NP at 0 K. Absolute zero is justified as the Planck law denies the NP the heat capacity to change in temperature consistent with the constituent NP atoms absent thermal motion.

IV. APPLICATION

The laser heated graphene flake [3] differs from the NP in that the heat Q focused at the center of the graphene layer flows in-plane and outward (red arrows) through the graphene to heat sinks as depicted in Fig. 3.
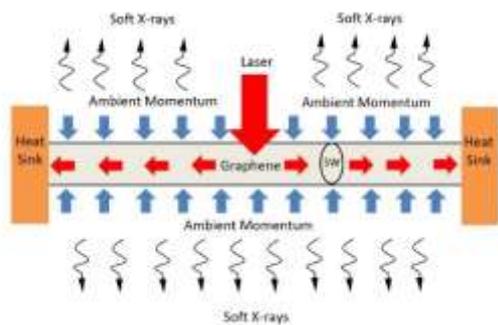

Figure 3. Laser heating of Graphene Flake

Along the graphene length, the heat flows by the Fourier law as EM confinement in the range of a few microns allows a classical treatment. However, the Planck law requires heat flow across the graphene thickness to be only EM radiation at soft X-ray levels. as illustrated shown in Fig. 3.

The EM standing waves (SW) noted across the graphene thickness are placed under EM confinement by the inward ambient thermal momentum (blue arrows) from the difference in temperature between the thermal surroundings at 300 K and the graphene which may be considered at 0 K.

The EM radiation at soft X-ray levels given by the Planck energy E of simple QED radiation, $E = hc/2nd$. Since the refractive index of graphite [19] from 50 - 1000 eV is $n \sim 1$, the single atom graphene thickness $d = 0.337$ nm gives wavelength $2nd = 0.674$ nm and $E = 1.8$ keV which is near the short wavelength 3 keV limit of soft X-rays. The 1.8 keV fluoresces down to ~ 270 eV and excites the CK bands [20] of graphite as shown in Fig. 4.
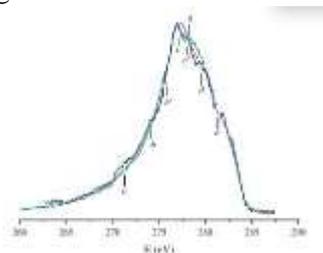

Figure 4. Soft X-ray emissions of carbons

Of importance is the significance of the soft X-ray emission in the enhancement of graphene thermal conductivity. Usually, simple QED only considers the minimum dimension of a nanostructure by Fermat's principle, the absorbed heat Q is dissipated in the least time which means in the direction of the shortest standing EM wave. By simple QED, the graphene flake has 3 quantum states characterized by EM waves standing across the thickness d, width w, and length L of the flake. The heat Q is dissipated by,

$$Q_d = hc/2nd$$
$$Q_w = hc/2nw$$
$$Q_L = hc/2nL$$

In the partitioning of heat Q in the flake, the ratio $Q_L/Q_d = d/L$ is of importance as the literature [2-7] assumes the heat loss $Q_d \ll Q_L$. In the experiment [3] shown in Fig. 1, the length L from the flake center to the trench edge is, $L = 1.5$ microns. For flake thicknesses $d < 1$ nm, $d/L < 0.0005$ which means little, if any, heat is conducted along the flake length. The heat Q is totally dissipated by soft X-ray emission.

Since flake lengths L of a few microns have finite heat capacity, the thermal conductivity along the length takes on bulk values $K \sim 2000$ W/mK. However, simple QED gives the ETC for the graphene flake, $ETC = K(d/L) \sim 1$ W/mK. Hence, reports [2-7] of nanoscale thermal conductivity from 4800 to 5800 W/mK are falsely overstated.

V. CONCLUSIONS

The Planck law denies atoms in graphene layers the heat capacity to conserve heat across the thickness by an increase in temperature. Phonons depending on temperature do exist along the length of a few microns, but not through the < 1 nm graphene layer.

Simple QED based on the Planck law conserves heat Q across graphene layers by the emission of EM radiation at ~ 280 eV soft X-ray levels.

Assuming laser heat is conducted in-plane to the heat sinks is false as virtually all heat is loss by soft X-rays before ever reaching the sinks. MD and FEM programs ANSYS and ABAQUS based on classical physics are not valid at the nanoscale.

High thermal conductivity of graphene at the nanoscale does not exist as assuming all laser heat flows in-plane through the layer to heat sinks is invalid. In fact, the ETC of graphene layers vanishes in the same way as for silicon NWs.

The 100X lower thermal conductivity of silicon NWs at the nanoscale compared to bulk is determined experimentally by measuring the temperature difference across the wire length. Graphene experiments should do the same.

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